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ENTHALPY OF VX HYDROLYSIS IN AQUEOUS SODIUM HYDROXIDE SOLUTION AT 90 °C

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PREFACE

The work described in this report was authorized by the U.S. Army Program Manager for Alternative Technologies and Approaches (PMATA). The work was started in May 2003 and completed in July 2003. The data are recorded in U.S. Army Edgewood Chemical Biological Center (ECBC) laboratory notebook 03-0108.

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ENTHALPY OF VX HYDROLYSIS IN AQUEOUS SODIUM HYDROXIDE SOLUTION AT 90 °C

1. INTRODUCTION

The chemical warfare agent O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (VX) is a persistent, colorless, and extremely toxic liquid.^a VX (M.W. = 267.36, d. = 1.008 g/mL at 25 °C) is a pentavalent organophosphorous ester that irreversibly inhibits the enzyme acetylcholinesterase (AChE) through phosphorylation of serine hydroxyl.^{b,c,1,2} The routes of exposure can be through inhalation, ingestion, and percutaneous contact. The function of AChE is to catalyze the hydrolysis of acetylcholine, the neurotransmitter, which generates a postsynaptic action potential that initiates organ activity.^{1,2,3} Accumulation of acetylcholine causes excessive organ activity and, eventually, death due to respiratory paralysis.^{1,2,3}

The reaction rate, products, and ratio of products of VX hydrolysis under basic conditions are pH and temperature dependent. The hydrolysis of VX in neutral to weakly basic solution at 23 °C results in two major P(V) products, O-ethyl methylphosphonic acid (a) and S-(2-diisopropylaminoethyl) methylphosphonothioic acid (b), and a minor P(V) product – O-ethyl methylphosphonothioic acid (c).^{d,4} However, the ratio of products as determined by ³¹P NMR for VX (1.0 wt %) heated in water for 2 h was 40/20/40 for a, b, and c, respectively.⁴ The kinetic rate of hydrolysis at 23 °C versus pH fits the equation $k_{\text{obs}} = k_i + k_{\text{OH}}[\text{OH}^-]$ with $k_{\text{OH}} = 5.19 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ to pH 13.⁴

The hydrolysis of VX in strongly basic solution provides only P(V) products a and b.⁴ As the concentration of hydroxide is increased from 0.5 M to 4.0 M, the ratio of a to b decreases.⁴ O-ethyl methylphosphonothioic acid is quite stable at room temperature, but can be hydrolyzed at a moderate rate ($t_{1/2} = 35.0 \text{ min}$) in 2.0 M hydroxide at 75 °C.⁴

The Program Manager for Alternative Technologies and Approaches (PMATA) has selected a hot caustic hydrolysis process for the neutralization of militarized VX. In the process, VX will be pumped into a stirred reactor containing 20.4 wt % NaOH solution at 90 °C. Several studies to support the process have been completed.^{5,6,7,8,9}

^a Typically physical properties of VX are as follows: ICT₅₀ (50% of exposed human population will be incapacitated) = 25 mg X min/m³ and LCT₅₀ (50% of the exposed human population will die without treatment) = 50 mg X min/m³ for percutaneous vapor exposure; ICT₅₀ = 5 mg/70 kg man and LCT₅₀ = 10 mg/70 kg man for percutaneous liquid exposure; Freezing point < -51°C, Vapor pressure 0.093 Pa @ 25 °C, and volatility = 10.5 mg/m³ @ 25 °C. MIL-HDBK-783 (EA), Chemical and Biological (CB) Contamination Avoidance and Decontamination, 15 October 1990.

^b M.W. is molecular weight and d. is density.

^c VX is not a refractory compound like GD, which “ages” (monodealkylation) rapidly after reacting with acetylcholinesterase. Reactivation (dephosphorylation) of the VX inhibited enzyme is possible if the antidote is administered quickly.

^d S-(2-diisopropylaminoethyl) methylphosphonothioic acid is extremely toxic. The compound is about 3.5 times less toxic than VX.

Under the reaction conditions (*supra vide*), VX hydrolyzes initially to the salts of **a**, **c**, 2-diisopropylaminoethyl mercaptan (**d**), and ethanol.^{e,5} Compound **c** reacts further to methylphosphonate and **d**.⁵ Additional characterization of the reactions included q_r , C_{pr} , and the heat transfer parameters.

Further characterization of the thermodynamics for the PMATA reaction is provided in this report. The ΔH , U_{Final} , and $C_{pr(Final)}$ were determined for two new ton container lots of munitions VX and the data compared statistically to previous values.

2. EXPERIMENTAL METHODS

2.1 Materials.

VX-S-6228-CTF-N-2 (purity = 82.0 area %, assayed 4 June 2003 by GC/MS) containing 0.8 area % dicyclohexylcarbodiimide (DCCDI) and VX9009-36903-05 (purity = 93.7 area %, assayed 19 June 2003) containing 4.9 area % diisopropylcarbodiimide (DICDI) were obtained from the Chemical Transfer Facility. Sodium hydroxide (lot # 966778) was purchased from Fisher Scientific Company (Newark, DE). Water was taken from the laboratory tap; the water was not assayed.

2.2 Equipment.

The enthalpy was measured in a Mettler-Toledo RC1 Reaction Calorimeter. The calorimeter system consisted of a glass-jacketed 2-liter reactor with glass baffle, an overhead agitator motor with impeller, a heat transfer reservoir, dosing controller, metering pump, and a constant temperature circulation bath. The process was controlled by Mettler-Toledo GmbH, WinRC V7.11 for RC1, Revision 800, software (Copyright© 2001). The WinRC1 software was run on a Dell OptiPlex GX200 computer with a Windows NT Workstation, Version 4, operating system. The Applied Test Team wrote a process template specifically for this study.

2.3 Reaction Calorimeter Tests.

VX (O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate) was added to aqueous sodium hydroxide (20.4 wt % or 5.01 M) at 90 °C in a 2-Liter reactor. Typically, VX was feed into the sodium hydroxide solution at 11.35 g/min. Stirring with a four-bladed 2" Rushton turbine radial flow impeller was maintained at 950 rpm, and a nitrogen purge was used to eliminate CO₂ from the reactor during the reactions. The virtual volume and calorimetric measurements were determined before and after the addition of VX.^f Reaction conditions were maintained for two hours after the addition of VX, then a sample was assayed by GC/MS to determine the extent of reaction. The ΔH , U_{Final} , and $C_{pr(Final)}$ were calculated by the WinRC1 software.

^e These were the principle products. Other products included ethyl methylphosphonothioic acid, Bis-[2-(diisopropylamino)ethyl] disulfide, and Bis-[2-(diisopropylamino)ethyl] sulfide.

^f Mettler-Toledo provides several technical manuals that describe the RC1 reactor, software, temperature measurements, and the treatment of data.

3. RESULTS

Reactions of acetic anhydride in water were used to calibrate the Mettler calorimeter. The ΔH for the reactions ($n = 3$) was $\bar{x} = 55 \text{ kJ S}_{N-1} 1.8/\text{mole}$ of acetic anhydride, which was similar to previous measurements.⁵ VX-S-6228-CTF-N-2 ($\bar{x} = 680.2 \text{ g S}_{N-1} 4.1$) was added to aqueous sodium hydroxide ($\bar{x} = 1377.1 \text{ g S}_{N-1} 5.4$) at 90°C . The feed rate was 11.35 g/min . The calculated ΔH for the reactions ($n = 9$) was $-139.6 \text{ kJ (S}_{N-1} 4.2) / \text{mole VX}$. In another set of reactions, VX9009-36903-05 ($\bar{x} = 599.8 \text{ g S}_{N-1} 0.4$) was added to aqueous sodium hydroxide ($\bar{x} = 1207.7 \text{ g S}_{N-1} 0.6$) at the same rate. The average enthalpy for the reactions ($n = 3$) was $-141.2 \text{ kJ (S}_{N-1} 4.7) / \text{mole VX}$. The values were calculated based on the assumption that the purity of the agents was 100%. There was no significant difference in ΔH for the two sets of reactions ($P_{\text{value}} = 0.5894$ at $\alpha = 0.05$).^g A previous study reported that the enthalpy for the reaction ($n = 3$) was $-143.3 \text{ kJ (S}_{N-1} 2.8) / \text{mole VX}$.^{5, h, i} The previous reported ΔH was not significantly different than the values obtained in the VX-S-6228-CTF-N-2 ($P_{\text{value}} = 0.1913$ $\alpha = 0.05$) and VX9009-36903-05 ($P_{\text{value}} = 0.5425$ $\alpha = 0.05$) reactions. The reaction data are provided in Table 1. Equations for the thermodynamic quantities are provided in Table 2.

The heat transfer coefficient (U) was determined at 85°C and 90°C before and after dosing with VX. In this study only the 90°C value obtained after the addition of VX is reported. The average U_{Final} for the VX-S-6228-CTF-N-2 reactions ($n = 8$) was $178.3 \text{ (W/(m}^2 \text{ }^\circ\text{K)) S}_{N-1} 7.7$. The value was significantly smaller ($P_{\text{value}} = 0.023$ $\alpha = 0.05$) than U_{Final} obtained from the VX9009-36903-05 reactions ($191.8 \text{ (W/(m}^2 \text{ }^\circ\text{K)) S}_{N-1} 5.6$). The U_{Final} for the VX-S-6228-CTF-N-2 reactions was also significantly lower ($P_{\text{value}} = 0.0012$ $\alpha = 0.05$) than the previous reported value $203.5 \text{ W/(m}^2 \text{ }^\circ\text{K)) S}_{N-1} 8.8$.⁵ There was no statistical difference between the previous reported U_{Final} and the value obtained from the VX9009-36903-05 reactions.

The $C_{\text{pr (Final)}}$ for the reactions with VX-S-6228-CTF-N-2 was $3.6 \text{ kJ/(kg }^\circ\text{K)) S}_{N-1} 0.2$. The quantity was not significantly different ($P_{\text{value}} = 0.4281$) than the average $C_{\text{pr (Final)}}$ for the VX9009-36903-05 reactions ($3.5 \text{ kJ/(kg }^\circ\text{K)) S}_{N-1} 0.1$). The previously reported value $3.6 \text{ kJ/(kg }^\circ\text{K)) S}_{N-1} 0.15$ ⁵ was not significantly different than the $C_{\text{pr (Final)}}$ for the VX-S-6228-CTF-N-2 and VX9009-36903-05 reactions ($P_{\text{value}} = 0.89$, $F_{\text{value}} = 0.117$ and $F_{\text{critical}} = 3.89$, ANOVA using Microsoft Excel).

^g The statistical results were obtained from a Student's t-Test calculator available at graphpad.com. The two-tailed P-values are for unpaired data.

^h The agent used in the study was VX-S-5166-CTF-N-15, purity = $87.1 \pm 2 \text{ wt } \%$, assayed by GC/FID with an internal standard.

ⁱ The reactants were 20 wt % sodium hydroxide ($1197.97 \text{ g} \pm 2.5$) and VX ($605.73 \text{ g} \pm 0.2$).

Table 1. Data for the Hydrolysis of VX in 20.4 wt % Aqueous Sodium Hydroxide at 90 °C

REACTION NUMBER	AGENT LOT/ STABILIZER	AMOUNT OF VX (g)	AMOUNT OF NAOH SOLUTION (g)	ΔH (kJ/mole VX)	U_{FINAL} (W/(m ² °K)) (90 °C)	$C_{PR(FINAL)}$ (kJ/(kg °K)) (90 °C)	[VX] 2h
M-1-01-VN-3156	VX-S-6228-CTF-N-2 (DCCDI)	669.2	1377	-148.38	179.5	3.63	^b <MDL
M-2-01-VN-3160	VX-S-6228-CTF-N-2 (DCCDI)	681.6	1377	-138.50	179.3	3.59	<MDL
M-3-01-VN-3161	VX-S-6228-CTF-N-2 (DCCDI)	681.2	1375	-138.95	168.7	3.41	<MDL
M-4-01-VN-3162	VX-S-6228-CTF-N-2 (DCCDI)	681.2	1377	-134.93	NA	3.25	<MDL
M-5-01-VN-3163	VX-S-6228-CTF-N-2 (DCCDI)	681.3	1374	-136.57	178.6	3.57	<MDL
M-6-01-VN-3167	VX-S-6228-CTF-N-2 (DCCDI)	681.6	1375	-137.10	165.2	3.38	20 ppm
M-7-01-VN-3168	VX-S-6228-CTF-N-2 (DCCDI)	682.0	1391	-137.41	182.4	3.70	<MDL
M-8-01-VN-3173	VX-S-6228-CTF-N-2 (DCCDI)	681.8	1375	-140.39	185.3	3.70	<MDL (3 h)
M-9-01-VN-3175	VX-S-6228-CTF-N-2 (DCCDI)	681.5	1373	-143.76	187.4	3.83	<MDL
M-11-01-VN-3181	VX9009-36903-05 (DICI)	599.3	1208	-140.31	192.8	3.54	<MDL
M-12-01-VN-3182	VX9009-36903-05 (DICI)	600.0	1208	-146.23	196.8	3.44	<MDL
M-13-01-VN-3183	VX9009-36903-05 (DICI)	600.0	1207	-136.95	185.7	3.57	<MDL
MT-1-01-VN-3156 through MT-9-01-VN-3175		^a \bar{x} = 680.2 S_{n-1} = 4.1	\bar{x} = 1377.1 S_{n-1} = 5.4	\bar{x} = -139.6 S_{n-1} = 4.2	\bar{x} = 178.3 S_{n-1} = 7.7	\bar{x} = 3.6 S_{n-1} = 0.2	NA
MT-11-01-VN-3181 through MT-13-01-VN-3183		\bar{x} = 599.8 S_{n-1} = 0.4	\bar{x} = 1207.7 S_{n-1} = 0.6	\bar{x} = -141.2 S_{n-1} = 4.7	\bar{x} = 191.8 S_{n-1} = 5.6	\bar{x} = 3.5 S_{n-1} = 0.1	NA

^aFinal values have been rounded-off to nearest tenths. ^bMDL is minimum detection limit (10 µg/mL) of GC/MSD. PPM is parts per million. NA is either not applicable or not available.

Table 2. Formulas for the Calculations of Heat Terms

$\Delta H = \int (Q_r - Q_b) \cdot dt$		
ΔH :	Reaction enthalpy	kJ
Q_r :	Heat generation rate, Σ of selected heat flow terms	kJ
Q_b :	Baseline for Q_r	kJ
$U = Q_f / (T_r - T_a)(A)$		
U :	overall heat transfer coefficient of the reactor wall	$W/(m^2 \text{ } ^\circ K)$
Q_f :	heat flow through the reactor wall	W
A :	heat exchange area (wetted area)	m^2
T_r :	temperature of the reactor contents	$^\circ C$
T_a :	corrected temperature of the reactor contents	$^\circ C$
$C_{pr} = Q_a / m_r (dT_r/dt)$		
C_{pr}	specific heat capacity of the reaction mass	kJ/(kg $^\circ K$)
m_r :	reaction mass (sum of all additions and dosings)	kg
dT_r/dt :	current change in the temperature of the reactor contents	K/s

4. CONCLUSIONS

The reaction of VX in aqueous sodium hydroxide (5.01 M) at 90 $^\circ C$ was more exothermic than the hydrolysis of acetic anhydride. The ΔH or q_r for the reaction with VX-S-6228-CTF-N-2 was statistically similar to the VX9009-36903-05 reaction, although the purity was dissimilar. Apparently, the q_r for the reactions of sodium hydroxide with the impurities was equivalent to the reaction with VX.

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